

Dependence of RIP(K) and RIP(N) of natural and urban sorbents on K⁺ and NH₄⁺ concentration

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Abstract. The technique of Waters et al. [4] was modified using a range of K⁺ and NH₄⁺ concentrations (from 0.1 to 16 mM dm⁻³) instead of the fixed K⁺ concentration (0.5 mM dm⁻³). The plot of K_d⁻¹ of ¹³⁷Cs vs K⁺ or NH₄⁺ concentration gives a single line or two lines depending on the material studied. The Langmuir-like competitive sorption isotherm equation was proposed to describe the product of ¹³⁷Cs distribution coefficient K_d on the competitive monovalent cation M⁺ concentration C_M. Main parameters of the equation are the maximal radiocesium interception potential RIP(M)_{max} and the affinity constant B(M). The K_dC_M value is designated as RIP(M). The Langmuir-like equation satisfactorily describes the dependence of RIP(M) on C_M. When two types of adsorption sites participate in the ¹³⁷Cs selective sorption process simultaneously the ¹³⁷Cs selective sorption can be described by RIP(M)_{max} and the affinity constant for high and low affinity sites, respectively. The high affinity sites are associated with the increased capacity of specific sorption sites at low C_M. This was indirectly confirmed by the effect of the reducing the ¹³⁷Cs exchangeable fraction with a decrease in C_M.

1. INTRODUCTION

Selective sorption of ¹³⁷Cs is the main mechanism affecting its behavior in mineral sorbents including nonorganic soils. It is generally accepted that when the regular exchange sites are masked by the excess, for example of Ca²⁺, ¹³⁷Cs specific sorption takes place at the frayed edge sites (FES) of the illite type clay minerals. The main cations M⁺, which compete with ¹³⁷Cs, are K⁺ and NH₄⁺. Such bivalent cations as Ca²⁺ and Mg²⁺ are believed to have no access to the FES due to the steric reasons [1]. The postulates used in the deriving the equations relating the distribution coefficient of ¹³⁷Cs K_d with M⁺ are the independence of the FES capacity on M⁺ concentration and application of the regular ion exchange laws to the ¹³⁷Cs and M⁺ reactions on FES [2, 3]. The following equation is widely used to describe the dependence of the K_d ¹³⁷Cs on C_M:

$$K_d = \frac{K_c^{FES}(Cs/M) \cdot [FES]}{C_M} \cdot Z_M^{FES}, \quad (1)$$

where K_c^{FES}(Cs/M) is the selectivity coefficient between trace quantities of Cs⁺ and M⁺ on FES, [FES] is the FES capacity, Z_M^{FES} is the fractional loading of

M^+ on FES. If we denote the product of $K_c^{FES}(Cs/M)$ on [FES] as a radiocesium interception potential in relation to the competitive cation M^+ RIP(M), and assume that the value of Z_M^{FES} equals 1 (providing the $C_{Cs} \ll C_M$, which is true for the environmental levels of ^{137}Cs), we obtain a simple and widely used equation:

$$K_d = \frac{RIP(M)}{C_M} \quad (2)$$

That is, K_d of ^{137}Cs directly proportional to the RIP(M) and inversely proportional to the concentration of a competitive cation M^+ . The RIP(M) is usually determined by the plateau value of the plot of the $K_d C_M$ vs C_M , or by the determination of the FES capacity and $K_c^{FES}(Cs/M)$ value, or by equating the $K_d C_M$ product to the RIP(M) at specified conditions as in the simplified method of RIP(M) determination proposed by Waters et al. [4]. The RIP(M) value is a valuable parameter as it gives the straightforward way of determining the K_d value. However, the equation (2) is derived for M^+ concentrations from about one to several mM dm⁻³. Moreover, if the plateau can be more or less easily determined for such a clay mineral as illite, the plateau value for clinoptilolite which has no specific sorption sites like FES but has marked selectivity due to the developed microporosity is difficult to determine.

An alternative approach can be proposed to determine the ^{137}Cs selective sorption. It consists in using the linearization procedure of K_d dependence on C_M in a narrow C_M range to fit Langmuir-like equation and on this basis predicting ^{137}Cs sorption in the more wide C_M range.

The approach of Wuster et al. [5] can be used to describe the competitive sorption of Cs^+ and M^+ by the Langmuir-like equation but assuming that the maximal selective sorption of cesium X_{max} equals that of M^+ :

$$X_{Cs} = \frac{B(Cs) \cdot C_{Cs}}{1 + B(M) \cdot C_M + B(Cs) \cdot C_{Cs}} \cdot X_{max}, \quad (3)$$

where X_{Cs} is the amount of sorbed Cs^+ , C_{Cs} is the Cs^+ concentration, $B(M)$ and $B(Cs)$ are the affinity constants of M^+ and Cs^+ , respectively. Dividing both sides of the equation (3) on C_{Cs} and transforming, we obtain:

$$\frac{1}{K_d} = \frac{1 + B(M) \cdot C_M + B(Cs) \cdot C_{Cs}}{X_{max} \cdot B(Cs)} \quad (4)$$

For ^{137}Cs , we can assume that $C_{Cs} \rightarrow 0$ and $B_{Cs} \cdot C_{Cs} \rightarrow 0$, therefore:

$$\frac{1}{K_d} = \frac{1}{X_{max} \cdot B(Cs)} + \frac{1}{X_{max} \cdot \frac{B(Cs)}{B(M)} \cdot C_M} \quad (5)$$

Denoting $X_{max} \cdot \frac{B(Cs)}{B(M)} = RIP(M)_{max}$, where $RIP(M)_{max}$ is the maximal radiocesium interception potential, mM kg⁻¹, we obtain the linear form of the Langmuir-like equation:

$$\frac{1}{K_d} = \frac{1}{RIP(M)_{max} \cdot B(M)} + \frac{1}{RIP(M)_{max}} \cdot C_M \quad (6)$$

From this equation it follows that the dependence of K_d^{-1} from C_M is described by a straight line. The angle of the slope is equal to $1/RIP(M)_{max}$, and

the intercept on the ordinate axis is equal to $1/(RIP(M)_{\max}B(M))$. Denoting K_dC_M as $RIP(M)$ we obtain:

$$K_d \cdot C_M = RIP(M) = \frac{B(M) \cdot C_M}{1 + B(M) \cdot C_M} \cdot RIP(M)_{\max} \quad (7)$$

That is, when $C_M \rightarrow \infty$

$$K_d = \frac{RIP(M)_{\max}}{C_M} \quad (8)$$

Equation (8) is equivalent to the equation (2). When $C_M \rightarrow 0$

$$K_d = B(M) \cdot RIP(M)_{\max} \quad (9)$$

The derived equations are valid for the scenario when FES capacity is a constant and does not depend on C_M . Let us consider the second possible scenario when FES capacity is not a constant but varies as a result of the potassium depletion from the interlayers of clay minerals at low C_M . There are no straightforward proof of the phenomenon at the environmental concentrations of cations but Sawhney [6] and Tamura [7] showed that the removal of K^+ from the interlayer spaces of biotite and illite with a tetraphenylborate solution increased the sorption of Cs^+ . The indirect evidence of the interlayers expansion and increasing the ^{137}Cs access to the specific sorption sites is the exchangeable fraction of ^{137}Cs (α_{Ex}). Smith and Comans [8] showed the increase of α_{Ex} in bottom sediments of the freshwater lake with increasing NH_4^+ concentration (C_N). De Koning and Comans [9] postulated the existence of the threshold C_N when illite interlayers are in complete collapse and α_{Ex} as determined by 1 M ammonium acetate extraction does not change with increasing C_N . The α_{Ex} can be an indicator of the amount of ^{137}Cs trapped inside the clay mineral interlayers thus showing indirectly the degree of change of specific sorption sites capacity.

The goal of this study is to check the equations presented above to describe the K_d dependence of the selectively sorbed ^{137}Cs in natural sorbents and such urban materials as granite and concrete on K^+ and NH_4^+ concentrations at sufficiently high background concentration of Ca^{2+} . Another goal was to simultaneously determine the dependence of α_{Ex} in the sorbents studied on C_K and C_N .

2. MATERIALS AND METHODS

2.1 Materials

The following sorbents have been studied: Fithian illite (ILLITE) (Illinois, USA), CH clinoptilolite (CLINOPT) (Teaque Mineral Product, Oregon, USA), tripolite (TRIPL) from Zikeevo deposit and dark-cherry bentonite (BENT) from Fersikovo deposit of Kaluga region, RF; granite (GRAN) and concrete (CONCR) were supplied from IPA USA in the frame of the ISTC project 4007. The sorbents were ground in a porcelain mortar and sieved through a sieve with a mesh diameter of 0.25 mm. Table 1 summarizes some properties of the sorbents studied. References in which properties are described are provided in brackets after the corresponding value.

The actual ($pH(H_2O)$) and exchangeable ($pH(KCl)$) acidity were determined by known procedures [10]. The cation exchange capacity (CEC) was determined by the $BaCl_2$ method at pH 6.5 [11]. The metal content was determined using the procedure accepted by the Hydrometeorological Service of the RF [12]. The values

of lost on ignition (LOI) was determined at 1000 °C, RIP(K) and RIP(N) was determined according [4].

Table 1. Physicochemical properties of the sorbents studied, on absolute dry weight.

	CLINOPT	ILLITE	BENT	TRIPL	GRAN	CONCR
RIP(K), mM kg ⁻¹	1798±2.5	7740±54	5860±2.40	3136±35	204±22	185±5
RIP(N), mM kg ⁻¹	2700±1.30	1242±32	1183±2.9	582±10	11.4±0.9	195.4±1.5
CEC, cM(+)kg ⁻¹	45.8±1.6	20.2±1.2	24.9±1.8	29.2±2.5	5.9±0.6	-
pH(H ₂ O)	7.3	5.4	7.4	3.8	10.0	12.3
pH(KCl)	5.2	4.9	6.8	4.3	9.7	12.5
CaO, %	0.98 [13]	0.51 [14]	0.12	1.2 [15]	17.39	4.12
MgO, %	0.20 [13]	3.31 [14]	1.60	0.3-0.9 [15]	0.54	1.90
BaO, %	-	-	0.02	-	0.16	0.03
K ₂ O, %	4.78 [13]	5.78 [14]	0.13	0.6-2.0 [15]	3.21	0.92
Na ₂ O, %	1.41 [13]	0.32 [14]	-	-	6.74	0.75
Al ₂ O ₃ , %	11.4 [13]	22.18 [14]	29.48	4.5 [15]	16.05	7.71
Fe ₂ O ₃ , %	2.15 [13]	9.08 [14]	5.81	2-3.5 [15]	1.29	3.95
MnO, %	0.02 [13]	-	0.02	-	0.01	0.04
SiO ₂ , %	66.5 [13]	46.96 [14]	-	-	-	-
TiO ₂ , %	0.32 [13]	-	-	-	-	-
LOI, %	6.24±0.03	7.31±0.03	9.07±0.01	3.64±0.03	0.238±0.01	11.26±0.01

2.2 Determination of RIP(M) and α_{Ex} as a function of C_M by the batch method

To determine the RIP(M) values we used the batch method suggested by Wauters et al. [2] modified to study the influence of the concentration of the competing cation M⁺. The sorbents (0.2 g) were placed in polycarbonate centrifuge tubes. Samples were preequilibrated three times with 50 cm³ of a solution containing 100 mM dm⁻³ Ca²⁺ and K⁺ (0.5-16 mM dm⁻³) or NH₄⁺ (0.125-16 mM dm⁻³) during 24 hours. After each equilibration the phases were separated by centrifugation and the liquid phase was discarded. Then 50 cm³ of a similar solution containing 1 kBq of ¹³⁷Cs was added to the centrifuge tube, and the suspension was shaken on to-and-fro shaker for 24 hours (¹³⁷Cs stock solution contained 0.2 kBq of CsNO₃ per kBq of ¹³⁷Cs). After centrifugation the ¹³⁷Cs specific activity in the liquid phase was determined on a Wizard 1480 gamma-counter with NaI(Tl) crystal detector. The RIP(M) values were calculated by the formula:

$$RIP(M) = \frac{V(C_0 - C_e)C_M}{m_S C_e}, \quad (10)$$

where C_0 is the initial specific activity of ^{137}Cs in solution, kBq dm^{-3} , C_e is the equilibrium specific activity of ^{137}Cs in solution, kBq dm^{-3} , V is the solution volume, dm^3 , m_S is the sorbent mass, kg, and C_M is the M^+ concentration in solution, mM dm^{-3} . The experiments were performed at 22 ± 2 °C for natural sorbents, and 20 ± 1 °C for urban materials.

The exchangeable fraction of selectively sorbed ^{137}Cs α_{Ex} was determined by extraction of a sorbent left after the determination of RIP(M) in the centrifuge tube with a 1 M ammonium acetate solution for 1 hour. The α_{Ex} value is the ratio of the ^{137}Cs activity in the 50 cm^3 of 1 M ammonium acetate solution and the sorbed ^{137}Cs activity.

3. RESULTS AND DISCUSSION

The results of the dependence of the ^{137}Cs selective sorption on C_M are shown in Fig. 1. Its indicate that the linear dependence of K_d^{-1} in the C_K range from 0.5 to 16 mM holds for clinoptilolite, illite and granite (Fig. 1a). The dependence of K_d^{-1} of ^{137}Cs on the NH_4^+ concentration for illite and clinoptilolite (Fig. 1b) as well as bentonite and tripolite is not linear but can be described by two straight lines. One of these lines describes the concentration range from 0 to ≤ 3 mM (curves 2 and 4), and the other, the concentration exceeding 3 mM (curves 1 and 3). This dependence suggests the presence of two types of selective sorption sites: high affinity sites (H) are filled at low C_N , and low affinity sites (L), at high C_N . The maximal radiocesium interception potentials $RIP(N)_{\max}^H$ and $RIP(N)_{\max}^L$ and the corresponding affinity coefficients $B(N)^H$ and $B(N)^L$, respectively, can be attributed to these sorption sites.

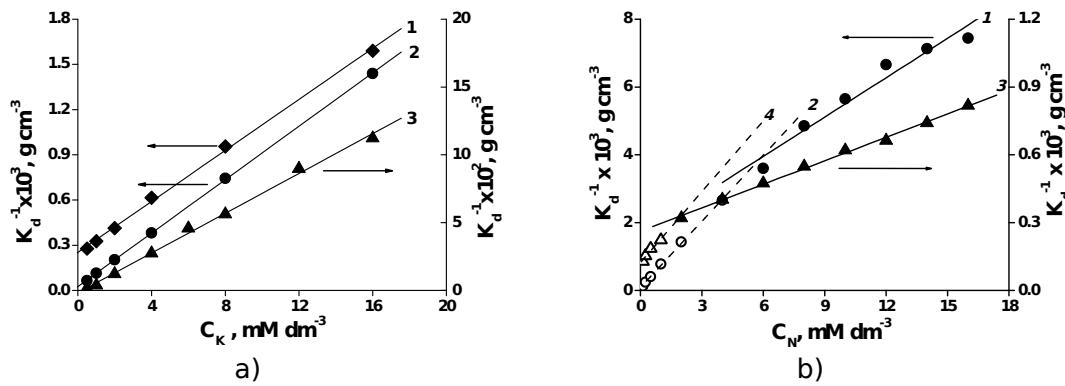


Figure 1. a) Plot of K_d^{-1} of ^{137}Cs vs. K^+ concentration: (1) clinoptilolite, (2) illite, (3) granite. b) Plot of K_d^{-1} of ^{137}Cs vs. NH_4^+ concentration: (1, 2) illite (3, 4) clinoptilolite; see also comments in the text.

The $RIP(M)_{\max}^H$ and $RIP(M)_{\max}^L$ and the corresponding affinity coefficients for both competing cations are given in Table 2.

Table 2. The values of $RIP(M)_{\max} \times 10^{-3}$ (mM kg^{-1}) and $B(M)$ ($\text{dm}^3 \text{ mM}^{-1}$) for natural and urban sorbents, on absolute dry weight.

	CLINOPT	ILLITE	BENT	TRIPL	GRAN	CONCR
$RIP(K)_{\max}$	11.81 ± 0.23	11.31 ± 0.05	-	-	136 ± 3	-

B	0.336 ± 0.02 3	3.4 ± 0.5	-	-	4.0 ± 3.1	-
RIP(K) _{max} ^H	-	-	8.5 ± 0.4	5.6 ± 0.1	-	224 ± 10
B(K) ^H	-	-	3.4 ± 0.9	$2.43 \pm 0.$ 18	-	5.8 ± 2.3 ±
RIP(K) _{max} ^L	-	-	$13.9 \pm 0.$ 4	8.9 ± 0.4	-	539 ± 50
B(K) ^L	-	-	$0.30 \pm 0.$ 04	$0.36 \pm 0.$ 07	-	$0.23 \pm 0.$ 07
RIP(N) _{max} ^H	9.6 ± 1.4	1.54 ± 0.0 3	$1.41 \pm 0.$ 07	$0.69 \pm 0.$ 03	-	-
B(N) ^H	0.84 ± 0.18	7.6 ± 2.2	$16.8 \pm 8.$ 3	$10.9 \pm 2.$ 0	-	-
RIP(N) _{max} ^L	28.9 ± 0.6	2.59 ± 0.2 7	$2.16 \pm 0.$ 13	$1.54 \pm 0.$ 09	-	-
B(N) ^L	0.13 ± 0.01	0.24 ± 0.0 9	0.9 ± 0.5	$0.53 \pm 0.$ 16	-	-

For illite, the RIP(N)_{max}^H and RIP(N)_{max}^L are considerably lower (1.5 and 2.5 M kg⁻¹) than for clinoptilolite (9.5 and 29.9 M kg⁻¹, respectively). However, these sorbents differ very strongly in the affinity coefficients B(N)^H and B(N)^L (7.6 and 0.24 dm³ mM⁻¹ for illite, 0.85 and 0.13 dm³ mM⁻¹ for clinoptilolite). These trends confirm the considerably higher affinity of ¹³⁷Cs for illite compared to clinoptilolite [3].

According to the Fig 1b illite exhibits the highest affinity for ¹³⁷Cs at high ¹³⁷Cs loadings (low M⁺ concentrations). The sorption sites with high affinity is expected to be filled first and the total sorbent affinity for ¹³⁷Cs will decrease with increasing ¹³⁷Cs sorption. However, high ¹³⁷Cs affinity at low C_M suggests a change in the properties of the sorbent. The high ¹³⁷Cs affinity is supposed to be the result of an increase in the number of selective sorption sites due to the depletion of potassium from the illitic mineral interlayers at low C_M. The concentration dependence of ¹³⁷Cs adsorption on C_M can be assessed indirectly by determining the exchangeable ¹³⁷Cs fraction Φ_{Ex}. If the amount of ¹³⁷Cs selective sites increases when C_M decreases then Φ_{Ex} value will be decreasing. The most convenient way of comparing the dependence of Φ_{Ex} on C_M for different sorbents is to use the ratio of the ¹³⁷Cs exchangeable fraction Φ_{Ex}(C_{M=n}), where n is the numerical value of C_M (mM dm⁻³) to the Φ_{Ex} at C_M = 16 mM dm⁻³, when the clay mineral interlayers can be postulated to be in the complete collapse. The dependence of the ratio 1 - Φ_E(C_{K=n})/Φ_E(C_{K=16}) is shown on Fig. 2. It can be seen that the 1 - Φ_E(C_{K=n})/Φ_E(C_{K=16}) for all sorbents increases considerably at low C_K indicating the possibility of increasing the number of selective sorption sites.

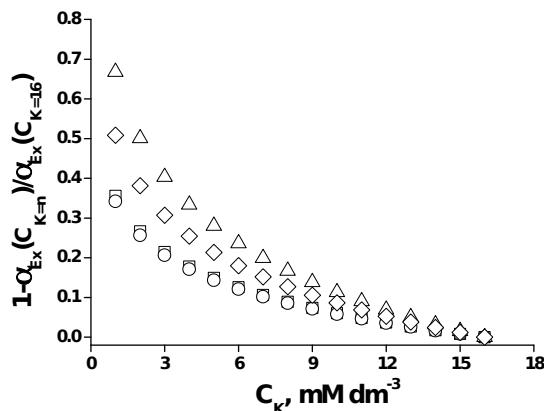


Figure 2. Normalized exchangeable fraction of selectively sorbed ^{137}Cs as a function of the K^+ concentration:
 \triangle - granite; \bullet - concrete; \square - illite; \circ - tripolite.

4. CONCLUSIONS

The mechanistic approach is proposed to describe the dependence of ^{137}Cs selective sorption on K^+ or NH_4^+ concentration using the competitive Langmuir-like equation. This equation relates the product of $C_M K_d$ (or the radiocesium interception potential relative the competing cation M^+ , $\text{RIP}(M)$) with the maximal radiocesium interception potential $\text{RIP}(M)_{\max}$ and affinity constant $B(M)$. The product $C_M K_d$ is denoted as $\text{RIP}(M)$ because the K_d value can be calculated at any C_M .

Two types of the K_d^{-1} relationships on C_M have been observed for natural sorbents. The linear dependence of K_d^{-1} in the C_K range from 0.5 to 16 mM holds for clinoptilolite, illite and granite. The dependence of K_d^{-1} of ^{137}Cs on the NH_4^+ concentration for illite and clinoptilolite, bentonite and tripolite can be described by two straight lines.

Sorbents exhibit the highest affinity for ^{137}Cs at high ^{137}Cs loadings (low M^+ concentrations). However, high ^{137}Cs affinity at low C_M suggests a change in the properties of the sorbent. The high ^{137}Cs affinity at low C_M is supposed to be the result of an increase in the number of selective sorption sites due to the depletion of potassium from the illitic mineral interlayers. This possibility is indirectly confirmed by the decrease of the exchangeable ^{137}Cs fraction α_{Ex} with a decrease in C_M .

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